Journal of Power Sources 280 (2015) 476–482

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Controllable synthesis of hierarchical SnO_2 microspheres for dye-sensitized solar cells

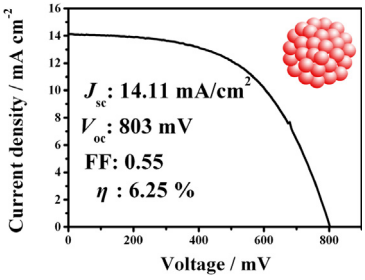
Yu-Fen Wang [a], Xi-Fei Li [a, *], De-Jun Li [a, *], Yuan-Wei Sun [b], Xian-Xi Zhang [b, *]

[a] Energy & Materials Engineering Centre, College of Physics and Materials Science, Tianjin Normal University, Tianjin 300387, China
[b] Shandong Provincial Key Laboratory of Chemical Energy Storage and Novel Cell Technology, School of Chemistry and Chemical Engineering, Liaocheng University, Liaocheng 252059, China

HIGHLIGHTS

- $Sn_6O_4(OH)_4$ microspheres intermediates can be successfully fabricated via a sonochemical process.
- Hierarchical SnO_2 microspheres were further obtained after $Sn_6O_4(OH)_4$ calcinations treatment at different temperatures.
- Different SnO_2 microspheres based DSSCs were investigated by *J–V* and CIMPS/IMVS.
- DSSCs based on S2 yielded a power conversion efficiency of 6.25%.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 18 November 2014
Received in revised form
7 January 2015
Accepted 19 January 2015
Available online 22 January 2015

Keywords:
Dye-sensitized solar cells
Microspheres
SnO_2
Sonochemical synthesis

ABSTRACT

Three-dimensional hierarchical SnO_2 microspheres were successfully synthesized through a rapid sonochemical reaction followed by a facile solvothermal process. The resultant samples were characterized in detail by X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM). It was observed that the hierarchical SnO_2 microspheres (~2.2 μm) consist of nanoparticles (~23–30 nm). These samples are used to fabricate photoelectrodes for dye-sensitized solar cells (DSSCs). The effects of different samples on the photovoltaic performance were studied based on photocurrent-voltage (*J–V*), intensity-modulated photocurrent spectroscopy (IMPS) and intensity-modulated voltage spectroscopy (IMVS). It is found that the highest power conversion efficiency of 6.25% has been achieved based on the hierarchical SnO_2 microspheres film photoanode with thickness of ~13.5 μm, and the corresponding photovoltaic parameters are 14.11 mA cm^{-2} in short-circuit current density, 803 mV in open-circuit voltage and 0.55 in fill factor, respectively.

1. Introduction

Since dye-sensitized solar cells (DSSCs) were firstly reported in 1991 by O'Regan and Grätzel [1], it has been regarded as one of the most promising candidates for future photovoltaic application owing to its low-cost and relatively high energy-conversion efficiencies [2]. So far, more than 13% power conversion efficiency was reported by optimization of photoanodes, sensitizers and electrolytes [3]. The photoelectrode is one of the most important components in DSSCs, which normally comprised of mesoporous wide-band-gap oxide semiconductor films with an high internal surface

* Corresponding authors.
E-mail addresses: xfli2011@hotmail.com (X.-F. Li), dejunli@mail.tjnu.edu.cn (D.-J. Li), xxzhang3@126.com (X.-X. Zhang).

http://dx.doi.org/10.1016/j.jpowsour.2015.01.115
0378-7753/

area [4]. Typically, the TiO_2 nanoparticles are utilized to generate nanopored structure on conductive oxide substrate [5], but the ultra-fast electron injection rates from the excited dye into the TiO_2 nanoparticles always conflict with the fast electron recombination rates due to low electron mobility properties and numerous trapping/detrapping sites for serious recombination [6]. To address this challenge, the other metal oxide semiconductors, such as ZnO, SnO_2, Zn_2SnO_4, have been recently investigated as promising photoelectrode of DSSCs.

Tin Oxide (SnO_2), as an important intrinsically n-type oxide semiconductor with the wide-band gap ($Eg = 3.8$ eV at 300 K), has received attractive attention originating from remarkable advantages of higher electron mobility (100–200 $cm^2\ V^{-1}\ S^{-1}$) [7] than TiO_2 (0.1–1.0 $cm^2\ V^{-1}\ S^{-1}$) [8], similar band-gap as TiO_2 (3.2 eV), low sensitivity to UV degradation [9] and great potential to further enhance the performance of DSSCs. In recent years, particular interest has been focused on improving the DSSCs efficiencies of SnO_2 nanoparticles by modifying electrode surface or coating of thin layer of other oxide materials [10,11].

It is worthy of being noted that another approach to increase efficiency is to enhance the light scattering by introducing scatterers into the top-layer of the photoelectrode film [12]. Normally, the submicrometer-sized particles as light scatters were introduced into the nanocrystalline films and thus leading to enhanced light-harvesting capability [13–16]. Unfortunately, the drawback is that the specific surface area decreased correspondingly for insufficient dye uptakes due to the introduction of large size particles. Therefore, it has raised considerable interest in finding a way to meet such conflicting requirements, for which hierarchical [16] structured films with submicrometer-sized aggregates assembled by nanocrystallines appear to be a promising choice. It has been demonstrated that such hierarchical structured materials have resulted in some efficiency improvements, for example, hierarchically structured TiO_2 [17–23] Zn_2SnO_4 [24] and ZnO [12,25]. Recently, Kuang et al. [26,27] reported the hierarchical structured octahedral (non-spherical) SnO_2 materials for the DSSCs application.

It is well known that the surface structure, size and shape are the main parameters determining the intrinsic properties of the metal oxide semiconductor materials [28]. Thus, unprecedented research efforts have been focused on the controllable preparation of micrometer- and submicrometer-crystals with nanoparticles. A lots of different approaches, such as surfactants [29], seeded growth [30,31] or the use of template materials [32], have been utilized to obtain tailored shapes as mentioned above. Among them, it is worth noting that the macromolecular precursors can be chemically transformed into new nanostructures, which is a convenient, versatile, and low-cost synthesis method of metal nanostructures by the polyol process [33,34]. Yang et al. [35] reported the hollow SnO_2 microspheres synthesized via hydrothermal process, but this needed a complex treatment as well as high energy cost. Thus, it is highly desirable to develop a facile, rapid and economical synthesis method for the preparation of hierarchically structured SnO_2 microspheres.

To address the aforementioned issues, we present a rapid and efficient ultrasonication-polyol process to synthesize $Sn_6O_4(OH)_4$ microspheres intermediates, and the hierarchical SnO_2 microspheres consisting of nanoparticles (~23–30 nm) were finally obtained after calcination in air for 3 h under different temperature ranged from 500 °C to 800 °C. The entire synthesis procedure is simple and consequently can be readily adopted to enlarge in this preparation. And we further report on TiO_2-coated SnO_2 microsphere as a photoelectrode material in DSSCs. It is found that the present DSSC based on hierarchical SnO_2 microspheres consisting of nanoparticles (calcination at 600 °C for 3 h) and N719 dye-sensitized exhibits a high power conversion efficiency of 6.25%.

2. Experimental

2.1. Synthesis

Hierarchical SnO_2 microspheres consisting of nanoparticles were successfully synthesized via a sonochemical process followed by calcination treatment at different temperatures. In a typical synthesis of $Sn_6O_4(OH)_4$ microspheres intermediates, $SnCl_2{\cdot}2H_2O$ was dissolved in the 1,2-propylene glycol, and the solution was stirred for 10 min. Then deionized water was added to this solution with stirring for 10 min. Afterwards, 1,2-ethylenediamine was added to this solution dropwisely and further stirred for another 10 min, and white suspension was obtained. Subsequently, the suspension was subjected to an intense ultrasonic irradiation (Sonics: VCX-500) for 10 min. The resulted precipitates were collected by centrifuging at 5000 rpm for 5 min and washed 3 times using absolute ethanol and distilled water, respectively, and finally dried at 60 °C. In order to obtain hierarchical SnO_2 microspheres, the as-prepared samples were calcinated in air at different temperatures (Typically, **S1**: 500 °C, 3 h; **S2**: 600 °C, 3 h; **S3**: 700 °C, 3 h; **S4**: 800 °C) for 3 h.

2.2. Preparation of the SnO_2 photoelectrodes

Firstly, the FTO glass (15 Ω/, Nippon Sheet Glass, Japan) was cleaned successively in water, ethanol, acetone using an ultrasonic bath for 15 min, and then rinsed with water and ethanol. And a thin compact of TiO_2 (~5 nm) was coated onto the FTO glass by spin coating TiO_2 sol–gel [36]. Briefly, titanium n-butoxide (34.2 mL) was added slowly into a solution containing acetylacetone (10.2 mL) and n-butanol (37.6 mL) under stirring. Hydrolysis of the clear mixture was then performed by the dropwise addition of an aqueous acidic solution (3.8 g paratoluenesulfonic acid in 18.0 mL H_2O). Stable transparent TiO_2 sol was obtained after heating the mixture solution at 60 °C for 12 h.

As forway of preparing a SnO_2 paste, 1.0 g of SnO_2 microspheres (without calcination) were ground for 40 min with the mixture of 8.0 mL ethanol, 0.2 mL acetic acid, 3.0 g of terpineol and 0.5 g of ethyl cellulose to form a slurry, and then the mixture were sonicated for 5 min in an ultrasonic bath. The paste was coated on the FTO glass coated with thin TiO_2 compact layer using the screen-printing technique. The thickness of SnO_2 film was controlled by repeated screen-printing times. And the electrodes coated with the SnO_2 pastes were gradually heated under an air flow at 325 °C for 5 min, at 375 °C for 5 min, at 450 °C for 15 min, and then at 500 °C for 15 min. The SnO_2 film were immersed into a 40 mM $TiCl_4$ aqueous solution at 70 °C for 30 min and washed with water and ethanol, then sintered at 520 °C for 30 min. After cooling down to room temperature, the fabricated SnO_2 electrodes was putted into anhydrous ethanol containing N719 dye (Ru[LL'-$(NCS)_2$], L = 2,2′-bipyridyl-4,4′-dicarboxylic acid, L = 2, 2′-bipyridyl-4, 4′-ditetrabutylammonium carboxylate, 5.0×10^{-4} M, Solaronix Co.), and was kept for 20 h at room temperature. The cell used for photovoltaic measurements consisted of a dye-adsorbed SnO_2 electrode, a counter electrode, a 60 μm thermal adhesive film (Surlyn, DuPont). The Pt-coated FTO as a counter electrode was prepared by dropping an H_2PtCl_6 (5.0×10^{-4} M) solution on the FTO glass followed by heating at 400 °C for 15 min in air. The electrolyte consisted of 1-propyl-3-methyl-imidazolium iodide (PMII, 0.6 M), I_2 (0.03 M), LiI (0.05 M), Guanidine thiocyanate (GuNCS) (GSCN, 0.1 M, Aldrich), and 4-tert-butylpyridine (t-BP, 0.5 M, Aldrich) in acetonitrile and valeronitrile (85:15 v/v). And electrolyte was filled from a hole made on the counter electrode, which was later sealed by